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PII: S0039-9140(17)30856-1
DOI: http://dx.doi.org/10.1016/j.talanta.2017.08.036
Reference: TAL17832

To appear in: *Talanta*

Received date: 11 May 2017
Revised date: 3 August 2017
Accepted date: 9 August 2017

Cite this article as: David Martínez, Daniel Torregrosa, Guillermo Grindlay, Luis Gras and Juan Mora, Coupling dispersive liquid-liquid microextraction to inductively coupled plasma atomic emission spectrometry: an oxymoron?, *Talanta,* http://dx.doi.org/10.1016/j.talanta.2017.08.036

Coupling dispersive liquid-liquid microextraction to inductively coupled plasma atomic emission spectrometry: an oxymoron?

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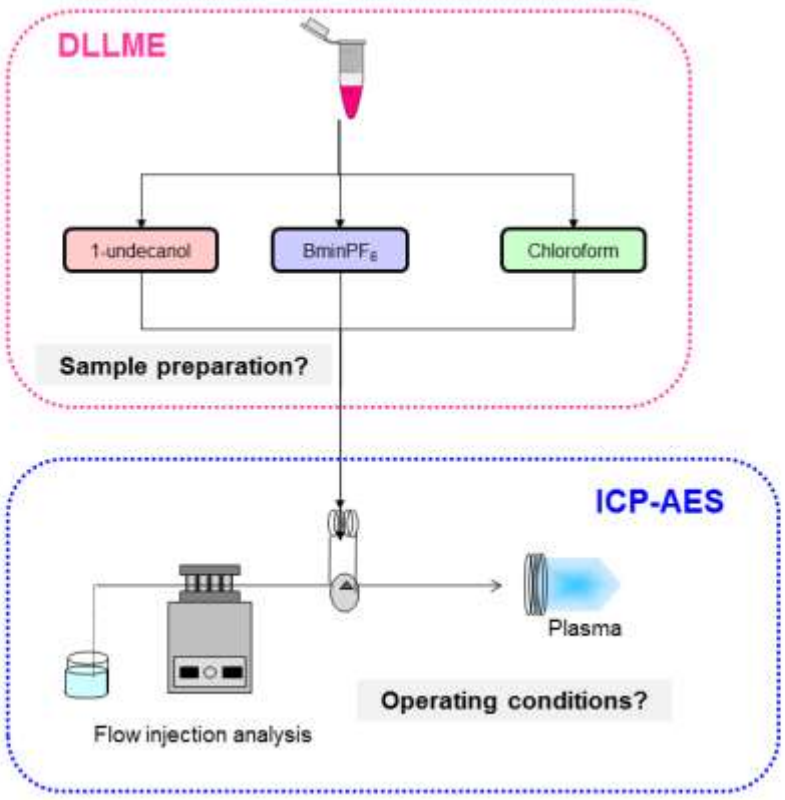
Abstract

Coupling dispersive liquid-liquid micro-extraction (DLLME) to inductively coupled plasma atomic emission spectrometry (ICP-AES) is usually troublesome due to the limited plasma tolerance to the organic solvents usually employed for metal extraction. This work explores different coupling strategies allowing the multi-element determination by ICP-AES of the solutions obtained after DLLME procedures. To this end, three of the most common extractant solvents in DLLME procedures (1-undecanol, 1-butyl-3-methyl-imidazolium hexafluorophosphate and chloroform) have been selected to face most of the main problems reported in DLLME-ICP-AES coupling (i.e., those arising from the high solvent viscosity and volatility). Results demonstrate that DLLME can be successfully coupled to ICP-AES after a careful optimization of the experimental conditions. Thus, elemental analysis in 1-undecanol and 1-butyl-3-methyl-imidazolium hexafluorophosphate extracts can be achieved by ICP-AES after a simple dilution step with methanol (1:0.5). Chloroform can be directly introduced into the plasma with minimum changes in the ICP-AES configuration

usually employed when operating with aqueous solutions. Diluted inorganic acid solutions (1% w w^{-1} either nitric or hydrochloric acids) have been successfully tested for the first time as a carrier for the introduction of organic extractants in ICP-AES. The coupling strategies proposed have been successfully applied to the multi-element analysis (Al, Cu, Fe, Mn, Ni and Zn) of different water samples (i.e. marine, tap and river) by DLLME-ICP-AES.



Keywords: metals, sample preparation, dispersive liquid-liquid microextraction, flow-injection, atomic emission spectrometry, inductively coupled plasma

1. Introduction

Dispersive liquid-liquid micro-extraction (DLLME) has been stablished as a fast and green sample preparation methodology to separate and preconcentrate analytes from samples with complex matrices [1]. Though most of the analytical applications reported in the literature have been focused on organic analytes, DLLME has also been employed for metal and non-metal analysis by means of spectroscopic techniques [2]. In these cases, detection is usually accomplished by means atomic absorption spectrometry (AAS) due to the robustness of the atomization sources (i.e. flame or furnace) and to the reasonably good analytical figures of merit [3,4]. Among the AAS techniques, electrothermal atomic absorption spectrometry (ETAAS) is often preferred because of the limited sample volume available after DLLME procedures. Nevertheless, its low sample throughput limits the application of the technique.

Inductively coupled plasma (ICP)-based techniques (i.e., ICP- atomic emission, ICP-AES, and ICP- mass spectrometry, ICP-MS) have a greater analytical potential than AAS techniques. ICP-based techniques allow simultaneous multi-element analysis, thus increasing sample throughput with minimum sample and reagent consumption as well as waste generation. However, due to the limited volume available after the microextraction procedure and low plasma tolerance to the organic solvents usually employed for analyte extraction [2,5], DLLME is not usually employed coupled to ICP-based techniques [6,7]. Thus, high volatile solvents (such as carbon tetrachloride, chloroform, etc.) have a deleterious effect on plasma conditions that negatively affects analytical figures of merit and could even lead to plasma extinction. Also, high viscous solvents (e.g. 1-

undecanol or ionic liquids), cause additional problems arising from a poor nebulization efficiency and strong memory effects. To address these shortcomings, several strategies have been suggested in the literature: (i) solvent evaporation and subsequent acid reconstitution before the analysis [8,9]; (ii) water back-extraction [10,11]; (iii) dilution with an appropriate solvent [12-15]; and (vi) the use of alternative sample introduction systems such as flow injection analysis (FIA) [16], electrothermal vaporization [17] or laser ablation [18]. Nevertheless, despite the above-mentioned approaches make feasible DLLME coupling to ICP-based techniques, some severe drawbacks still remain. In fact, the main inherent benefits of DLLME (e.g. simplicity, high sample throughput, etc.) are mostly counterbalanced due to the additional steps required to perform the analysis. Moreover, some approaches may require complex modifications in the ICP configuration that are not always available in most of the analytical laboratories.

From the above-mentioned considerations, it can be derived that DLLME-ICP-based techniques is a rather complex coupling and, hence, usually discarded from a practical point of view. However, a comprehensive review of the works reported in this field reveals that most of the previous studies have been mainly focused on the optimization of the extraction procedure. Nevertheless, no studies including the optimization of the experimental and instrumental conditions of the plasma source have been performed up to date. This is a very surprisingly fact taking into account the strong influence of the ICP parameters (e.g. plasma power, sample uptake rate, nebulizer gas flow rate, etc.) and the sample introduction system on the analytical figures of merit [5,19,20]. In our

opinion, to couple DLLME-ICP-based techniques, the optimization of the full variables (experimental and instrumental) of both DLLME and ICP is mandatory. The extensive number of applications based on the use of plasma-based techniques for elemental analysis in organic matrices [19] justify the interest of this coupling.

The goal of this work is to explore and evaluate different analytical approaches for coupling DLLME to ICP-AES. To this end, several organic solvents usually employed in DLLME procedures and covering different range of the main physical properties affecting the signal response in ICP-AES (i.e., viscosity and volatility) have been selected: 1-undecanol, 1-butyl-3-methyl-imidazolium hexafluorophosphate and chloroform. These solvents have been introduced (either directly or after a dilution step with alcohol or acid solutions) into the plasma source by means of a flow injection device. Main ICP-AES experimental variables (plasma r.f. power, nebulizer gas flow rate and carrier flow rate) have been also optimized to make feasible the analysis of these organic solvents by ICP-AES and to achieve the best analytical figures of merit. Finally, the proposed DLLME-ICP-AES approaches have been compared and evaluated by analyzing several water samples (i.e. marine, tap and river).

2. Experimental

2.1 Chemicals

Organic solvents (i.e., 1-undecanol, chloroform, 1-butyl-3-methylimidazolium hexafluorophosphate, acetone, methanol, absolute ethanol and 1-propanol) and chelating agents (i.e. diethyldithiocarbamate (DDTC), 2-theonyltrifluoroacetone

(TTA), ammonium pyrrolidine dithiocarbamate (APDC) and a multi-element 200 mg L^{-1} organometallic solution were purchased from Sigma-Aldrich (Steinheim, Germany). Sodium chloride, 69% w w^{-1} nitric acid, 36% w w^{-1} hydrochloric acid, 85% w w^{-1} phosphoric acid, sodium dihydrogen phosphate, acetic acid and sodium acetate were obtained from Panreac (Barcelona, Spain). An ICP-IV multi-element 1000 mg L^{-1} solution was provided by Merck (Darmstadt, Germany).

2.2 Solutions

Three different extractant solvents, namely: (i) 1-undecanol; (ii) 1-butyl-3-methyl-imidazolium hexafluorophosphate ($BmimPF_6$); and (iii) chloroform, have been evaluated. These solvents were selected, among the most common extractants in DLLME, to face most of the main problems arising from DLLME-ICP-AES coupling (e.g. solvent viscosity and volatility) (see Table 1) [21-23].

When operating with viscous solvents (1-undecanol or $BmimPF_6$), a dilution step prior to the analysis by ICP-AES was mandatory. Thus, 1-undecanol was diluted in different alcohols, namely, methanol, ethanol and 1-propanol. This approach was also employed for $BmimPF_6$ but, in this case, 36% w w^{-1} hydrochloric acid solution was additionally tested as a dilution solvent. Physical properties of the different dilution solvents employed for 1-undecanol and $BmimPF_6$ are also gathered in Table 1. Dilution ratios ranging from 1:0.5 to 1:3 for both 1-undecanol and $BmimPF_6$ were tested. Analyte standard solution in each media was prepared in two-steps. First, an aliquot of the aqueous 1000 mg L^{-1} ICP-IV multi-elemental reference solution was spiked into the proper

dilution solvent (i.e. methanol, ethanol, 1-propanol or 36% w w^{-1} hydrochloric acid solution). Next, this solution was mixed in the right proportion with 1-undecanol or $BmimPF_6$ for a final analyte concentration of 1 mg L^{-1}.

Chloroform-based samples were directly analyzed by ICP-AES. Therefore, analyte chloroform standard (1 mg L^{-1}) was prepared by diluting the appropriate aliquots of a 200 mg L^{-1} multi-elemental organometallic solution in this solvent.

2.3 Instrumentation

ICP-AES measurements were performed using an Agilent 720 ICP-AES (Agilent, Santa Clara, USA) with axial viewing using the operating conditions reported in Table 2. Different sample introduction systems were tested depending on the characteristics of the extractant solvent used. Thus, when operating with both 1-undecanol and chloroform, a standard sample introduction system made of a concentric pneumatic nebulizer (Seaspray, Glass Expansion, Australia) and a cyclonic spray chamber (Cinnabar, Glass Expansion, Australia) was used. As regards $BmimPF_6$, a micronebulizer (OneNeb, Ingeniatrics, Sevilla, Spain) coupled to a single-pass with impact bead PTFE spray chamber (Thermo Scientific, Germany) was employed. All the organic solvents were drived to the nebulizer by means of a V-451 flow injection manifold (Upchurch Scientific, Silsden, United Kingdom) equipped with a 25 µL loop valve. DLLME extracts were injected using a home-made 300 µL plastic syringe with PEEK coated quartz capillary needle (200 µm i.d., PEEKSIL, Upchurch, Oak Harbor, Washington, USA). Samples were introduced into a carrier stream controlled by

a peristaltic pump (Model Minipuls 3, Gilson, France). Different carriers were evaluated through this work: (i) 1% w w^{-1} HNO_3; (ii) 1% w w^{-1} HCl; and (iii) air. Signal acquisition was performed by means of the transient signal (TRS) software of Agilent's ICP-AES. Microsoft Excel® software was employed for manually signal integration. The wavelengths of the emission lines monitored in this work are listed in Table S1 (appendix).

2.4 Samples

Three water samples covering a wide range of matrix characteristics were tested: (i) tap water (University of Alicante); (ii) river water (Vinalopó river, N 38º28´15.0096", W 0º48'15.0336"); and (iii) marine water (Mediterranean Sea, N 38º22´31.7424", W 0º24'32.5224"). All samples were collected in polyethylene terephthalate bottles and, after a filtration step with a 0.45 µm syringe filter, acidified and stored at 4ºC until the analysis.

2.5 DLLME procedures

Three DLLME procedures for water analysis were employed to evaluate the different coupling strategies developed in the present work. Next, these methodologies are briefly described.

1-undecanol-based extraction

Metal extraction with 1-undecanol was carried out using the DLLME procedure described by Yamini et al. [12] with some minor modifications. A sample solution of 5 mL was placed into a 10 mL screw-cap and pH was adjusted using

an acetic acid-acetate buffer solution (pH: 6). Next, it was spiked with 600 µL of a 30 w v^{-1} NaCl solution and 25 µL of a 1 g L^{-1} TTA solution in methanol. Simultaneously, 50 µL of 1-undecanol were mixed with 500 µL of acetone and the mixture quickly injected into the sample solution by using a 5.0 mL of syringe. A cloudy solution was formed and, after a centrifugation step (5 min 4000 rpm), the sample solution was transferred into an ice bath where the 1-undecanol (≈45 µL) was solidified at the top of the top of the test tube. Finally, 1-undecanol was transferred into an Eppendorf tube where it was melted and diluted with methanol (1:0.5 ratio) before ICP-AES analysis.

BMIMPF$_6$-based extraction

In this procedure, based on that reported by Wen et al. [24], 5 mL of the sample were spiked with a phosphoric/dihydrogen phosphate buffer solution to adjust the pH (4). Next, 70 mg of NaCl and 100 µL of a 9% APDC solution added to the sample. A mixture of BmimPF$_6$ (150 mg) and methanol (600 µL) was injected into the sample to form a cloudy solution. The sample was then centrifuged (5 min 4000 rpm) and BmimPF$_6$ (settled at the bottom of the glass test tube) finally transferred into an Eppendorf tube, where it was diluted with methanol (1:0.5 proportion) before ICP-AES analysis.

Chloroform-based extraction

In this procedure, based on that previously described by Hemmatkhah et al. [25], 5 mL of water containing 3.5% w w^{-1} NaCl and 0.010 g DDTC were placed in a 10 mL screw cap glass tube with conical bottom. The solution pH was

adjusted to 6.0 with an acetic acid/acetate buffer solution. Next, 100 mg of chloroform were dissolved in 400 µL of ethanol and the mixture was injected into the glass tube containing the sample. A cloudy solution is formed and, after centrifugation (4000 rpm, 2 minutes), chloroform was sedimented at the bottom of the conical test tube. Chloroform was then transferred into an Eppendorf tube and directly analyzed by ICP-AES.

3. Results

3.1 Coupling 1-undecanol-based DLLME procedures to ICP-AES

3.1.1 Strategies for 1-undecanol introduction into the ICP

Direct analysis of 1-undecanol by ICP-AES is not a feasible task due to its high viscosity (17.2 mPa s^{-1}, see Table 1). As a consequence, this solvent cannot be properly displaced by the peristaltic pump, thus giving rise to poor signal reproducibility and high wash-out times. In addition, when operating with pneumatic nebulizers, high viscosity solvents generate coarser aerosols than the low viscous ones thus negatively affecting the aerosol transport into the plasma and, then, the analytical signal [5,26]. To solve these problems and make feasible the introduction of 1-undecanol solutions in ICP-AES, several strategies were evaluated. First, since solvent viscosity decreases with temperature, 1-undecanol was heated (from 40-70ºC) before being injected into the FIA system. Though sample pumping improved increasing the temperature, memory effects were still significant. Alternatively, PTFE tubing from the peristaltic pump to the nebulizer was also heated but no improvement was observed. A second approach reported in the literature to deal with 1-undecanol

matrix samples by ICP-AES is its dilution with alcohols [12,14]. Up to date, no systematic study about the influence of the alcohol nature and concentration used for 1-undecanol dilution have been carried out, in spite of the strong influence of the sample matrix on the analytical figures of merit in ICP-AES [5,27]. In the present work, methanol, ethanol and 1-propanol were investigated as dilution solvents for 1-undecanol. Different 1-undecanol:alcohol mixtures (ranging from 1:0.5 to 1:3) containing 1 mg L^{-1} analyte were prepared and measured by ICP-AES (Figure 1). In general, mixture composition did not have a significant influence on the analytical signal. Signals for the 1:0.5 and the 1:1 mixtures were very similar but their peak areas were around1.2-fold lower than those obtained for the 1:2 and 1:3 ones. Similar findings were observed when using ethanol and 1-propanol. These results suggest that alcohol dilution slightly improves the aerosol generation due to the reduction of the solution viscosity. Nevertheless, since the 1-undecanol dilution factor is not too high, no significant differences are expected between the different mixtures tested. From these experiments, the 1:0.5 mixture was selected for further analysis since it provides the minimum sample dilution after the DLLME treatment. The proposed dilution factor is lower than that previously reported in the literature (i.e., usually $\geq$ 1:1) [12,14]. In general, the type of alcohol employed to dilute 1-undecanol had a limited influence on the analyte emission signal (Figure 2). Emission signals obtained for the methanol mixture were about 15% higher, on average, than those obtained with ethanol or 1-propanol. This behavior was the expected considering the highest volatility of methanol (Table 1). Plasma robustness was checked by means of the Mg II (280.271 nm)/Mg I (285.213

nm) line intensity ratio for the different 1-undecanol/alcohol mixtures [28]. In all cases, Mg II/Mg I ratio were similar to that obtained for water, thus suggesting that the presence of 1-undecanol/alcohol mixtures did not affect plasma temperature.

Finally, the influence of the carrier nature on the signal obtained in DLLME-ICP-AES was also evaluated. Up to date, poor attention has been paid in the literature to optimize the FIA experimental conditions required for 1-undecanol analysis by ICP-AES, mainly regarding the nature of the carrier solution. In fact, with the exception of Yamini et al. [12] that report the use of 80% 1-propanol v v^{-1} as a carrier, no significant details about carrier characteristics are found in the literature [10]. Despite its potential interferences [29], acids are preferred over organic solvents in ICP-AES since they can be directly introduced into the plasma avoiding the use of complex instrumental arrangements (e.g. oxygen addition, desolvation, etc.) [19,27]. Nevertheless, no study reporting the use of acids as carrier solutions have been found for the analysis of DLLME extracts by ICP-AES. In the present work, 1% w w^{-1} nitric acid and 1% w w^{-1} hydrochloric acid solutions were tested as carriers instead of organic solvents for the first time. Results demonstrated that acid solutions can be successfully used to introduce 1-undecanol/alcohol mixtures into the plasma with high reproducibility and no memory effect. No differences between the signals afforded with both acids were registered.

3.1.2 Optimization of ICP-AES experimental conditions

Analytical figures of merit in ICP-based techniques strongly depend on plasma

experimental conditions. For this reason, the influence of the nebulizer gas (Q_g) and carrier flow rate (Q_l) on analyte signal was carried out. Plasma r.f. power was kept closed to maximum nominal value available with the instrument (1400 W) to favor analyte atomization and ionization. Figure 3 shows the influence of Q_g on Cd II 214.439 nm integrated emission signal for the 1:0.5 1-undecanol:methanol mixture at different Q_l values. Results indicate that the highest emission signals were obtained at Q_g of 0.7 L min^{-1}, irrespective of the Q_l tested. Moreover, results in this figure also indicate that the highest emission signals were obtained at the lowest Q_l employed. Thus, Cd II 214.439 nm integrated emission signal raises 2.3-fold when decreasing Q_l from 1.5 to 0.6 mL min^{-1} at the optimum Q_g. Similar results were observed for the different alcohol mixtures and analytes tested. This behavior can be explained in terms of aerosol generation and transport [26] and plasma characteristics [27]. Thus, the Mg II/Mg I ratios measured at 0.6 and 1.5 mL min^{-1} were of 6.0 and 5.0, respectively.

3.2 Coupling $BminPF_6$-based DLLME procedures to ICP-AES

3.2.1. Strategies for $BminPF_6$ introduction into the ICP

When operating with $BmimPF_6$, similar (or even worse) experimental drawbacks than those described for 1-undecanol are observed. In fact, the viscosity of $BmimPF_6$ is higher (about 22-fold higher) than that of 1-undecanol (Table 1). Therefore, a dilution step with an appropriate solvent previous to the $BmimPF_6$ solutions into the plasma is also mandatory. Following a similar approach used with 1-undecanol, $BmimPF_6$ could be diluted with methanol, ethanol and 1-

propanol in different proportions (ranging from 1:0.5 to 1:3). Different $BmimPF_6$:methanol mixtures (1:0.5 to 1:3) containing 1 mg L^{-1} analyte were measured to evaluate matrix influence on the signal. It was observed that when operating the 1:1 mixture, signal was about 60% higher than that obtained with the 1:0.5 one. Signals for the highest diluted $BmimPF_6$ ratios (1:2 or 1:3) were similar to those for the 1:1 ratio. These findings suggest the beneficial effects of the $BmimPF_6$ dilution on the aerosol generation due to the reduction of solution viscosity. This behavior is in agreement with the previous findings obtained with 1-undecanol but the influence of dilution on analyte emission signal for $BminPF_6$ was more significant due to its higher viscosity. The signal improvement registered for the 1:1 mixture did not compensate the analyte dilution factor expected when operating the 1:1 dilution instead of the 1:0.5 one (2-fold). Therefore, the 1:0.5 dilution was selected for further studies. As expected from the low dilution factors employed for $BmimPF_6$, no significant differences on analyte signals were registered operating the different $BmimPF_6$ mixtures (Figure S1, Appendix). Thus, for instance, the use of methanol as a diluent solvent provided the highest signals but signal improvement when compared to ethanol and 1-propanol was only 1.2 fold. This value is similar to that previously found with 1-undecanol.

Attempting to find alternatives to alcohols for $BmimPF_6$ dilution, the possibility of using hydrochloric acid was explored in this work for the first time. Preliminary experiments demonstrated that when mixing 1:1 $BmimPF_6$:concentrated hydrochloric acid (36 % w w^{-1}), a single phase was obtained after 4-5 hours at room temperature. Interestingly, the mixture viscosity was clearly lower than

that of the pure $BmimPF_6$. Several experimental evidences suggest that the structure of the ionic liquid is modified in the presence of hydrochloric acid. The ionic liquid/acid mixture has a brownish color similar to that of the hexafluorophosphoric acid solutions [30]. This compound is not stable in aqueous media and it is found in equilibrium with phosphoric acid, phosphoric conjugate forms and hydrofluoric acid [31]. Thus, assuming the formation of hexafluorophosphoric acid from the reaction between $BmimPF_6$ and hydrochloric acid, hydrofluoric acid must be formed. This hypothesis was clearly confirmed after checking a glass surface that was in contact with a 1:1 $BmimPF_6$:HCl mixture for 15 minutes. Finally, it was also observed that blank signals for DLLME extracts operating glass vials were systematically higher than those obtained operating plastic ones. The miscibility of $BmimPF_6$ with hydrochloric acid was further investigated by modifying acid concentration and $BmimPF_6$:acid ratio. Results indicate that $BmimPF_6$ was only miscible with concentrated hydrochloric acid, regardless the acid proportion employed (from 1:0.5 to 1:3). Finally, several strategies were tested to improve the miscibility kinetics between $BmimPF_6$ and hydrochloric acid. First, the different ionic liquid – hydrochloric acid mixtures were shaken either with a vortex or ultrasounds but unsuccessfully. Better results were obtained when heating the $BmimPF_6$/HCl mixture in Eppendorf tubes at temperatures between 40-70ºC. Operating this way, a single phase was obtained after heating the mixture at 70 ºC for 5 min (fast enough for practical purposes). It is worth to point out that concentrated nitric acid is also useful for $BmimPF_6$ dilution but it was discarded due to the flammability and oxidizing capabilities of $BmimNO_3$. Because of HF presence in

the $BmimPF_6$:acid mixture, the standard ICP-AES sample introduction system was replaced by a nebulizer and a spray made of PTFE. For the sake of comparison, this configuration was also employed with the experiments performed with $BmimPF_6$:alcohol solutions. Also the plasma torch is susceptible to be affected by the presence of HF. Nevertheless, after several hours operating $BmimPF_6$:hydrochloric acid mixtures no sign of HF attack was observed. Presumably, it was due to the low sample volume introduced and the system wash-out with the carrier solution. Although at first glance, physical properties of $BmimPF_6$:hydrochloric acid mixtures are expected to be less favorable for aerosol generation and transport, analyte signals for the $BmimPF_6$:acid mixtures were almost identical to those afforded by ethanol and 1-propanol (Figure S1, Appendix). Plasma robustness was examined for the different $BmimPF_6$ mixtures but no significant differences in the Mg II/Mg I intensity ratio were observed. In fact, the value obtained for this parameter was similar to that found when operating with water (and, hence, 1-undecanol:alcohol mixtures). Considering the above-discussed results, it seems to be clear that the use of hydrochloric acid for $BmimPF_6$ dilution does not afford any advantage against the use of alcohols. Moreover, the standard glass-made sample introduction system could be used instead of the PTFE since no HF is formed when diluting $BminPF_6$ with alcohols.

As regards the nature of the carrier solutions, similar to that observed with 1-undecanol, nitric acid and hydrochloric acid solutions can be employed as carriers for $BmimPF_6$ analysis. The use of inorganic acid solutions as carrier is clearly simpler and less prone to interferences than that previously proposed by

Ranjbar et al. [16] for metal analysis with 1-hexyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide (i.e. 80% v v-1 1-propanol solution). In fact, no significant memory effects were registered for the different diluted $BmimPF_6$ mixtures operating the acid carriers. Analyte wash out was similar to that obtained with 1-undecanol (25-30 s)

3.2.2. Optimization of ICP-AES experimental conditions

The influence of ICP experimental conditions (Q_g and Q_l) on the analyte signal (and plasma properties) obtained when operating with $BmimPF_6$ were analogous to those already shown for 1-undecanol (Fig. 2). Thus, despite of the use of a different sample introduction system, the optimum Q_g for $BmimPF_6$ was also found at 0.7 L min^{-1}. Interestingly, it was observed that the influence of Q_l on analyte signal was less significant than with 1-undecanol. Regardless the solvent employed for $BmimPF_6$ dilution, analyte signal rose approximately 1.6-fold when decreasing Q_l from 1.5 to 0.6 mL min^{-1}. This behavior can be attributed to the higher viscosity of $BmimPF_6$ mixtures regarding to 1-undecanol ones.

3.3 Coupling chloroform-based DLLME procedures to ICP-AES

3.3.1. Strategies for chloroform introduction into the ICP

Opposite to that occurring with 1-undecanol and $BmimPF_6$, the low viscosity of chloroform permits it to generate pneumatic aerosols with no additional dilution treatment. Nevertheless, the direct analysis of chloroform DLLME extracts by ICP-AES has been previously avoided in the literature due to the undesirable

effects caused by this solvent in ICP-AES (mainly signal instability and negative effects on the plasma excitation characteristics) [16]. Instead, additional pretreatments to remove chloroform have been recommended before metal analysis by ICP (e.g. back extraction, evaporation, etc.) [8-10,15]. In this work, however, it was noted that chloroform could be directly introduced in the ICP with the FIA manifold. The volume of chloroform introduced into the instrument (25 µL) was low enough to avoid carbon deposits and plasma shutdown. Nevertheless, it is important to note that plasma appearance was affected by the high solvent load consequence of the high chloroform volatility (e.g. green light emission from the C_2 band in the aerosol channel) [5]. With the goal of improving the analytical response, some minor changes were performed on the ICP-AES operating conditions employed with viscous solvents [19]. First, auxiliary gas flow was increased from 1.25 to 2.25 L min^{-1} thus improving plasma tolerance to organics [5]. On the other hand, Q_l higher than 1.0 mL min^{-1} were not employed to avoid plasma flickering. Operating on this way, there is not any experimental limitation to operate chloroform directly in ICP-AES thus taking advantage all the benefits of DLLME (e.g. sample throughput, simplicity, analyte enrichment factors, etc.).

3.3.2. Optimization of ICP-AES experimental conditions

In line with the strategy used with the viscous solvent, either 1% w w^{-1} nitric and hydrochloric acids were employed as carriers for chloroform. In addition, air was also tested since it could be advantageous for volatile solvent introduction into the ICP [32,33]. Figure 4 shows the results obtained for Cd II 214.439 nm

integrated emission signal using chloroform and both 1% w w^{-1} nitric acid and air as FIA carriers. Results for 1% w w^{-1} hydrochloric acid are not shown since they were similar to those obtained with the nitric acid solution. From results in Fig.4 it can be derived that emission signal strongly depends on the carrier employed. Thus, when operating air as carrier, Cd signals (Figure 4.B) were higher than those obtained for 1 % w w^{-1} HNO_3 (Figure 4.A), regardless the Q_l tested. These findings could be explained considering that when using air: (i) the analyte is not dispersed in the liquid stream, (ii) the spray chamber is kept dry between injection which in turns favor solvent evaporation and aerosol transport to the plasma; and (iii) analyte losses due to coalescence and aerosol turbulence are reduced. Nevertheless, from a practical point of view, the benefits of using air as a carrier were counterbalanced by the higher memory effects due to the lack of a solution to wash-out the system between samples during the analysis [32].

Fig.4 also shown that, in general, irrespective of the carrier used, the optimum Qg for Cd signal was also found at 0.7 L min-1 but this optimum value was more diffuse than that observed with viscous solvents (Fig.3). In fact, as it can be seen in Fig.4, a signal plateau was obtained between 0.6 and 0.7 L min-1 for some Ql values, especially when operating with air carrier. Finally, as expected, signal improved when decreasing Ql due to a better aerosol generation and transport and plasma characteristics [27]. It is interesting to note that differences between both carriers were reduced when decreasing Ql [33]. Thus, when Ql is decreased from 1.0 to 0.4 mL min-1, analyte signal ratio between air and nitric acid passed from 1.84 to 1.17-fold. To explain this behavior, it must

be considered that liquid evaporation is favored at low Ql values, thus improving analyte transport (i.e. less aerosol losses) and, hence, differences between air and liquid carriers are reduced. Though the use of air as a carrier afforded higher signals than the acid solutions, this approach was unattractive from a practical point of view due to memory effects. Opposite to that observed when operating viscous solvents, and despite the experimental changes made on the ICP setup, plasma characteristics were strongly deteriorated by the presence of chloroform. Thus, for a given set of experimental conditions, the MgII/MgI ratio was half of that obtained with water, 1-undecanol or $BmimPF_6$.

3.5 Analysis of real samples

The multi-element analysis (i.e., Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) of different water samples was performed to validate the strategies developed for coupling DLLME to ICP-AES. To this end, previously described DLLME procedures for 1-undecanol [12], $BmimPF_6$ [24] and chloroform [25] were employed for metal extraction in waters. Next, each organic extract was analyzed by ICP-AES under the optimum conditions obtained for each solvent (Table 3). Q_l was set at 0.4 mL min^{-1} for all the solvents tested to favor aerosol generation and plasma characteristics. Though better results are theoretically expected decreasing further this parameter, nebulization process becomes less stable [20] thus distorting the emission signal profile and reducing signal precision. Moreover, higher wash-out times were required compromising sample throughput.

Preliminary experiments showed that analyte extraction efficiency was strongly dependent on the water salt content and, hence, some changes in the extraction procedures were required. To study the influence of water salts (ionic strength) on analyte extraction for each DLLME procedure, 100 µg L^{-1} analyte standard solution containing variable amounts of NaCl from 0.1 to 7.5 % w w^{-1} were used. Results shown that each DLLME methodology is differently affected by NaCl. Thus, analyte extraction efficiency for the 1-undecanol-based DLLME procedure decreased with NaCl concentration. On the other hand, extraction efficiency showed a maximum at 3.5 % w w^{-1} NaCl when operating with chloroform. Interestingly, no influence of NaCl concentration on the analyte extraction efficiency was observed when using $BmimPF_6$. These results suggest that NaCl content (i.e. solution ionic strength) exerts a great influence on metal extraction since it affects both the solubility of the metal-chelate complex in the sample as well as the miscibility between the organics and water. From these experiments, it was clear the significance of controlling salt content to avoid interferences. Taking into account these findings, both standards and samples were spiked with NaCl 3.5% w w^{-1} for all the DLLME procedures to perform calibration using a single set of standards.

First, a recovery test was performed to evaluate the accuracy. To this end, all the samples were spiked with a multi-element standard solution for a final concentration of 100 µg L^{-1} and, then, they were analyzed by ICP-AES after the appropriate DLLME treatment. Results obtained are shown in Table 4. As it can be observed, recoveries for all the elements with 1-undecanol and chloroform were almost quantitative (i.e., recoveries ranging from 96 to 109%). However,

analyte recoveries for $BmimPF_6$ were only quantitative for Pb. It must be considered that the $BmimPF_6$-based DLLME procedure used in the present work was initially developed for Pb determination and, hence, results for this element were totally expected. The origin of the poor recoveries for the remaining elements could be partially related to pH influence on APDC chelating capabilities [34]. This topic, however, was not further investigated since it was beyond the scope of this work.

Table 5 shows the results of the elemental analysis of water samples obtained using the 1-undecanol and chloroform-based DLLME procedures. For the sake of comparison, the results obtained with a direct water analysis by ICP-AES are also included. Data for the $BmimPF_6$-based DLLME procedure are not included since it only worked for Pb and the concentration of this element was below LoD (<5 μg L^{-1}). In fact, none of the methodologies tested could detect Pb as well as Cd and Cr due to their low concentration levels in the samples analyzed. In general, results for the elemental analysis using DLLME procedures agree with those obtained using a direct analysis procedure. Nevertheless, the use of DLLME methodologies allowed the analysis of a higher number of elements (e.g. Al, Fe, etc.) in water samples due to their lower limits of detection (Table 6). In comparison with a direct water analysis, DLLME methodologies afford, on average, a LoD improvement of 8 and 13-fold when operating with 1-undecanol and chloroform, respectively. These results confirm the usefulness of the coupling strategies evaluated for the analysis of DLLME extracts by ICP-AES. It is important to remark that the improvement in the analytical figures of merit reported for DLLME-ICP-AES was related to two different factors: *(i)* the

preconcentrating process itself; and, *(ii)* the higher analyte transport efficiency afforded when using organic solvents in ICP-AES. To evaluate the contribution of aerosol generation and transport with organics on the analytical figures of merit (sensitivity and LoD), the corresponding calibration curve for organics and water were compared (Table S2, Appendix). The use of 1-undecanol and $BmimPF_6$ improved sensitivity and LoD 2.2-fold on average for the different elements tested. LoD improvement for chloroform was also similar (2.8-fold) but less than expected according to signal enhancement factors (6.5-fold on average) due to high blank signals originated by the chloroform impurities. Therefore, a higher improvement in LoDs for chloroform is still feasible improving reagent quality. Nonetheless, different commercial chloroform providers were tested but similar backgrounds were observed in all cases.

Conclusions

Results in this work clearly demonstrate that there is not any limitation for coupling DLLME to ICP-AES when experimental conditions are wisely selected. In fact, despite the different physical properties shown by the organic solvents usually employed in DLLME, a single set of experimental conditions can be employed for metal analysis. In addition, it should be taking into account that analytical figures of merit in ICP-AES are not only improved by the DLLME treatment process but also to aerosol generation and transport afforded by the organics regarding to water. When compared to FAAS and ETAAS detection, the use of ICP-AES makes feasible the simultaneous analysis of different metals thus improving sample throughput. In addition, internal standardization

calibration could be implemented to improve accuracy and precision as well as to mitigate potential matrix effected derived by the organics in the plasma.

It is expected that the strategies developed in this work could also be applied for ICP-MS. Nonetheless, special attention should be paid in this case to the spectral and non-spectral interferences due to carbon since ICP-MS is more sensitive to matrix effects. In fact, the use of organics could be beneficial to further improve the analytical figures of merit since the ionization of some hard-to-ionize elements (e.g. As, Se, etc.) is improved by carbon presence in the plasma [35]. These experiments are currently being carried out in our laboratories.

Acknowledgements

The authors would like to thank the Generalitat Valenciana (Project GV/2014/138) for the financial support of this work. D. Martínez and D. Torregrosa also thank the University of Alicante for the research fellowships (UAFPU2015-5998 and AII16-33).

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:...'.

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Figure captions

Figure 1. Cd II 214.439 nm emission signal profile for different 1-undecanol:methanol mixtures. (▲) 1:0.5; (●) 1:1; (■) 1:2; and (◆) 1:3. Q_g: 0.7 L min^{-1}; Q_l: 0.6 mL min^{-1}. FIA carrier: 1% w w^{-1} HNO_3.

Figure 2. Influence of the alcohol employed for 1-undecanol dilution on the integrated emission signal of several elements. Q_g: 0.7 L min^{-1}; Q_l: 0.6 mL min^{-1}; 1-undecanol/ alcohol ratio: 1:0.5; FIA carrier: 1% w w^{-1} HNO_3.

Figure 3. Influence of the nebulizer gas flow rate on Cd II 214.439 nm integrated emission signal operating 1:0.5 1-undecanol:methanol mixture at different Q_l. (◆) 0.6 mL min^{-1}; (▲) 0.9 mL min^{-1}; (●) 1.2 mL min^{-1}; and (■) 1.5 mL min^{-1}. FIA carrier: 1% w w^{-1} HNO_3.

Figure 4. Influence of the nebulizer gas flow rate on Cd II 214.439 nm integrated emission signal with chloroform at different sample uptake rate using 1% w w^{-1} nitric acid (A) and air (B) as FIA carriers. (◆) 0.4 mL min^{-1}; (▲) 0.6 mL min^{-1}; (●) 0.8 mL min^{-1}; and (■) 1.0 mL min^{-1}. FIA carrier: 1% w w^{-1} HNO_3.

Table 1. Physical properties of the organic solvents tested in this work at 25ºC.

	Surface tension (mN m^{-1})	**Viscosity (mPa s^{-1})**	**Density (g mL^{-1})[&]**	**Vapor pressure (mmHg)**

1-undecanol	26.5	17.2	0.83	0.0004
BmimPF$_6$	47.7	381	1.38	-
Chloroform	26.7	0.56	1.49	26.2
Methanol	22.7	0.54	0.79	128
Ethanol	22.0	1.07	0.79	59
1-propanol	20.9	1.95	0.80	21
HCl (36% w w^{-1})	65.8	1.84	1.6	35

[&]20ºC

Table 2. ICP-AES operating conditions

Agilent 720 ICP-AES	Solvent		
	1-undecanol	$BmimPF_6$	Chloroform
Plasma forward power (W)	1400		
Argon flow rate (L min^{-1})			
Plasma	15.0		
Auxiliary	1.25		2.50
Nebulizer	0.6-0.9		0.5-0.8
Carrier flow rate (mL min^{-1})	0.4-1.5		0.4-1.0
Sample introduction system			
Nebulizer	Seaspray®	Seaspray®/Oneneb®	Seaspray®
Spray chamber (material)	Cyclonic (Glass)	Cyclonic (Glass)/Single pass with impact bead (PFA)	Cyclonic (Glass)
Flow injection loop volume (µL)	25		
Acquisition time (s)/replicates	30/3		

Table 3. Optimum coupling strategies for the analysis of 1-undecanol, $BmimPF_6$ and chloroform extracts by ICP-AES.

Parameter	1-undecanol	$BmimPF_6$	Chloroform
Dilution Solvent	Methanol		-
Dilution ratio	1:0.5		-
Carrier	1 % w w^{-1} HNO_3		
Q_g (L min^{-1})	0.7		
Q_l (mL min^{-1})	0.4		

Table 4. Recoveries obtained for analyte spiked water samples using different DLLME procedures based on 1-undecanol, $BmimPF_6$ and chloroform extraction. ICP-AES: Q_g: 0.7 L min^{-1}, Q_l:0.4 mL min^{-1}. FIA carrier: 1% w w^{-1} HNO_3.

	Recovery values (%)								
	1-undecanol			BmimPF6			Chloroform		
Element	Sea	Tap	River	Sea	Tap	River	Sea	Tap	River
Al	102±4	99±2	100±4	<5	<5	<5	99±4	100±2	99±5
Cd	99±3	101±3	98±3	<5	14±10	14±10	103±3	102±3	109±3
Cr	97±5	97±4	98±3	<5	23±13	<5	100±1	103±3	99±3
Cu	100±3	98±4	98±3	<5	19±13	<5	98±3	99±3	98±2
Fe	99±4	98±4	98±4	<5	<5	<5	100±4	99±5	100±3
Mn	101±4	100±3	101±3	70±10	80±20	60±10	99±2	97±3	95±5
Ni	100±3	100±4	98±3	<5	15±9	14±7	99±4	98±4	102±3
Pb	99±5	96±5	98±4	99±5	96±6	96±7	98±4	97±3	99±2
Zn	100±2	98±4	100±4	<5	<5	<5	99±4	98±4	102±4

Table 5. Results of the analysis of water samples in ICP-AES using 1-undecanol and chloroform-based DLLME procedures as well as direct sample analysis (no preconcentration). ICP-AES: Q_g: 0.7 L min^{-1}, Q_l:0.4 mL min^{-1}. FIA carrier: 1% w w^{-1} HNO_3.

	Concentration (µg L^{-1})								
	Direct analysis			1-undecanol-DLLME			Chloroform-DLLME		
Element	Sea	Tap	River	Sea	Tap	River	Sea	Tap	River
Al	<150	215±14	<150	75±2	226±5	135±4	71±4	220±5	135±4

Cu	230±20	145±6	350±9	207±4	150±4	331±4	208±3	140±4	335±3
Fe	<90	<90	<LoD	61±4	59±5	23±3	64±2	57±1	24±5
Mn	240±20	<LoD	<LoD	238±3	<LoD	<LoD	229±3	<LoD	<LoD
Ni	400±5	130±7	140±12	407±2	111±5	140±2	410±5	110±3	136±3
Zn	100±15	85±7	<60	98±2	73±4	56±4	97±4	72±4	53±4

Precision is presented in form of confidence intervals obtained as *ts* where *t* is the Student's *t* (4.3 for a 95% confidence level) and *s* is the standard deviation of three replicates of the analysis

Table 6. Limits of detection (LoD) in ICP-AES for direct sample analysis and 1-undecanol and chloroform-based DLLME procedures. ICP-AES: Q_g: 0.7 L min^{-1}, Q_l:0.4 mL min^{-1}; 1-undecanol dilution: methanol; 1:0.5 ratio; FIA carrier: 1% w w^{-1} HNO_3.

	Limit of detection (µg L^{-1})		
Element	**Direct analysis**	**1-undecanol-DLLME**	**Chloroform-DLLME**
Al	50	6	35
Cd	30	6	1,4
Cr	40	6	6
Cu	30	2	7
Fe	30	4	4
Mn	40	22	6
Ni	30	8	0,7
Pb	20	4	1,1
Zn	20	3	2

Highlights

- DLLME coupling to ICP-AES is totally feasible
- Analysis of DLLME extracts is achieved under standard plasma conditions
- Chloroform is directly analyzed but a dilution step is required for viscous solvents
- Inorganic acid solutions could be employed as FIA carriers